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			5e. TASK NUMBER		
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14. ABSTRACT Many material improvements are needed for specific aerospace propulsion applications. Because the industrial community in extremely risk-averse, the responsibility to achieve significant advancements in this area falls largely to government laboratories. This presentation will discuss on-going materials research performed at the Air Force Research Laboratory, Rocket Propulsion Division, located at Edwards Air Force Base. Recent research activities focused on inert materials for solid rocket propulsion applications, including the development of alternative high-temperature thermosetting resins, will be described, as well as specialized applications for use in liquid rocket propulsion.					
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# Advanced Hybrid Materials for Propulsion Applications



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# Acknowledgements



Profs. Gareth McKinley & Bob Cohen  
*Superoleophobic Surfaces*



Professor Anish Tuteja  
*Oil/Water Separation Membranes*



Professor Dennis Smith  
*Fluorinated Compounds*



Polymer Working Group  
*Fluorinated Compounds*

*Financial Support*



*Air Force Office of Scientific Research  
AFRL, Aerospace Systems Directorate*



# Polymer Working Group



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***AFRL/RQR***

***AFOSR***





# Motivation

- Many hydrophobic surfaces exist in nature but there is no naturally occurring oleophobic surface
- Plenty of academic and commercial interest in the development of oleophobic surfaces
- Focus on commercially available textiles



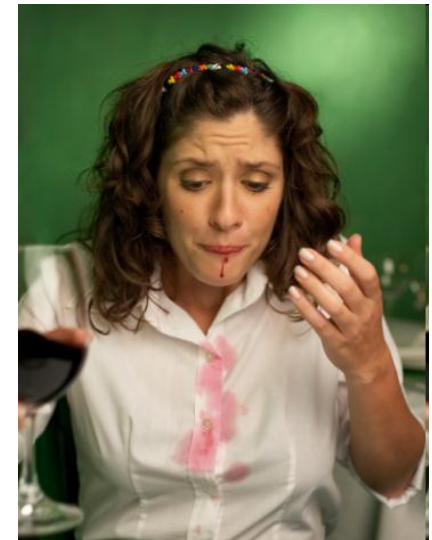
[www.thedailygreen.com](http://www.thedailygreen.com)



[www.gfn.com/sowhatyourpoint/wp-content](http://www.gfn.com/sowhatyourpoint/wp-content)



[www.defense-technologynews.blogspot.com](http://www.defense-technologynews.blogspot.com)

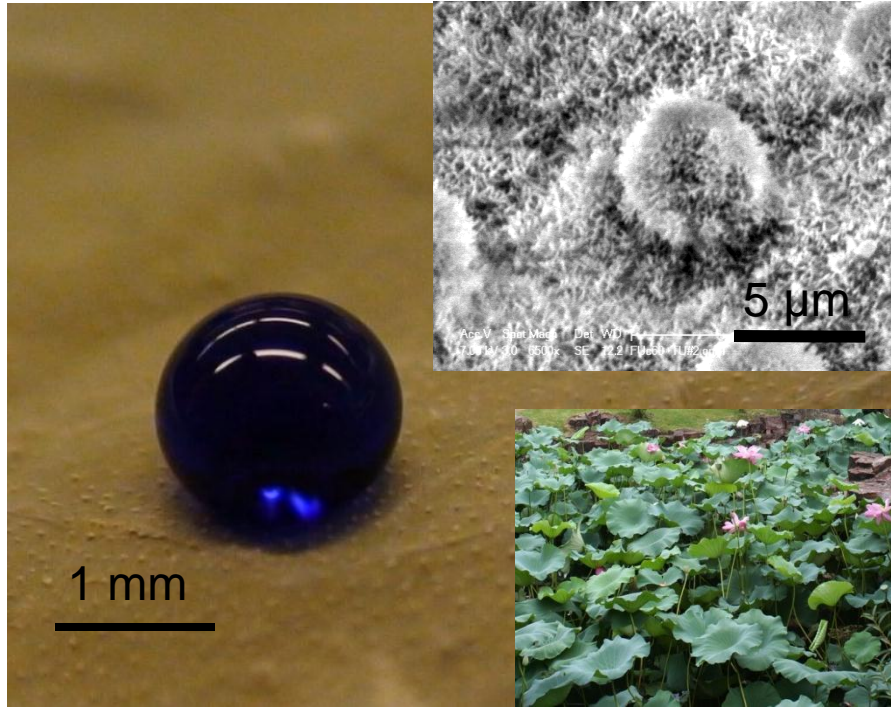


[www.tressugar.com](http://www.tressugar.com)





# The lotus leaf (*Nelumbo nucifera*)



Water,  $\gamma_{LV} = 72.1 \text{ mN/m}$

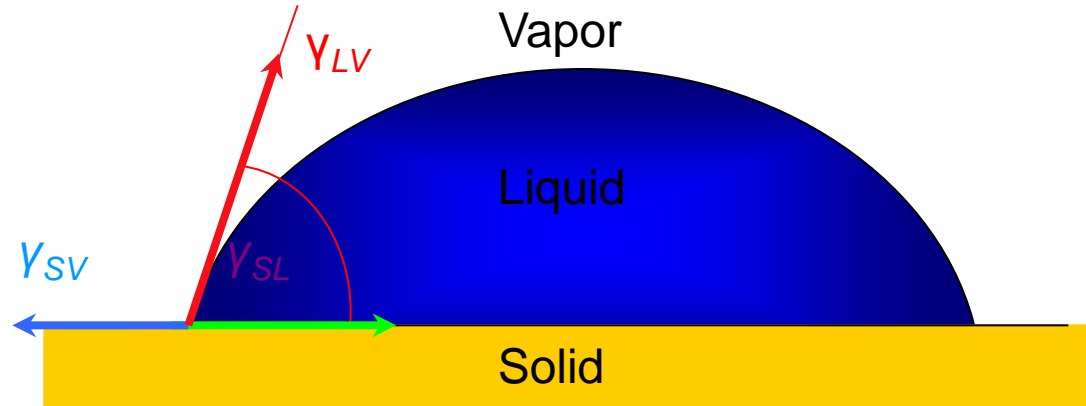


Hexadecane,  $\gamma_{LV} = 27.5 \text{ mN/m}$

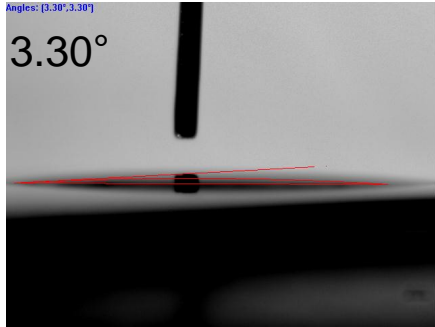
Previous research suggests that the superhydrophobicity of the lotus leaf is related to the low **surface energy** of the wax crystalloids covering the protruding nubs and its **surface roughness**.



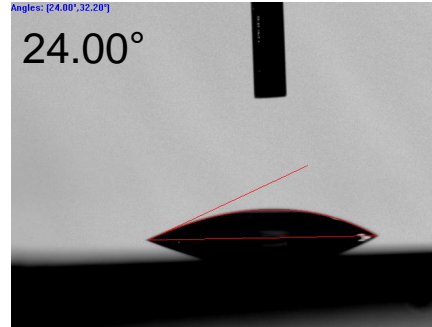
# Non-wetting surfaces



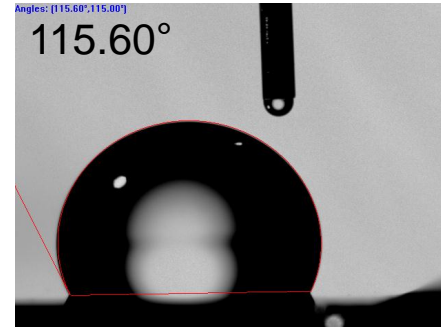
Contact angles with water:



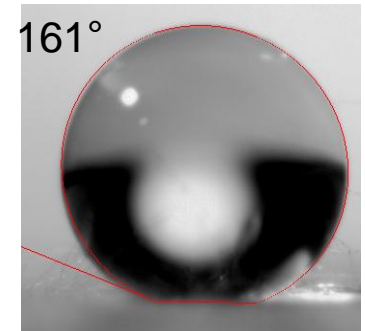
Superhydrophilic  
 $\theta \sim 0^\circ$



Hydrophilic  
 $0^\circ < \theta < 90^\circ$



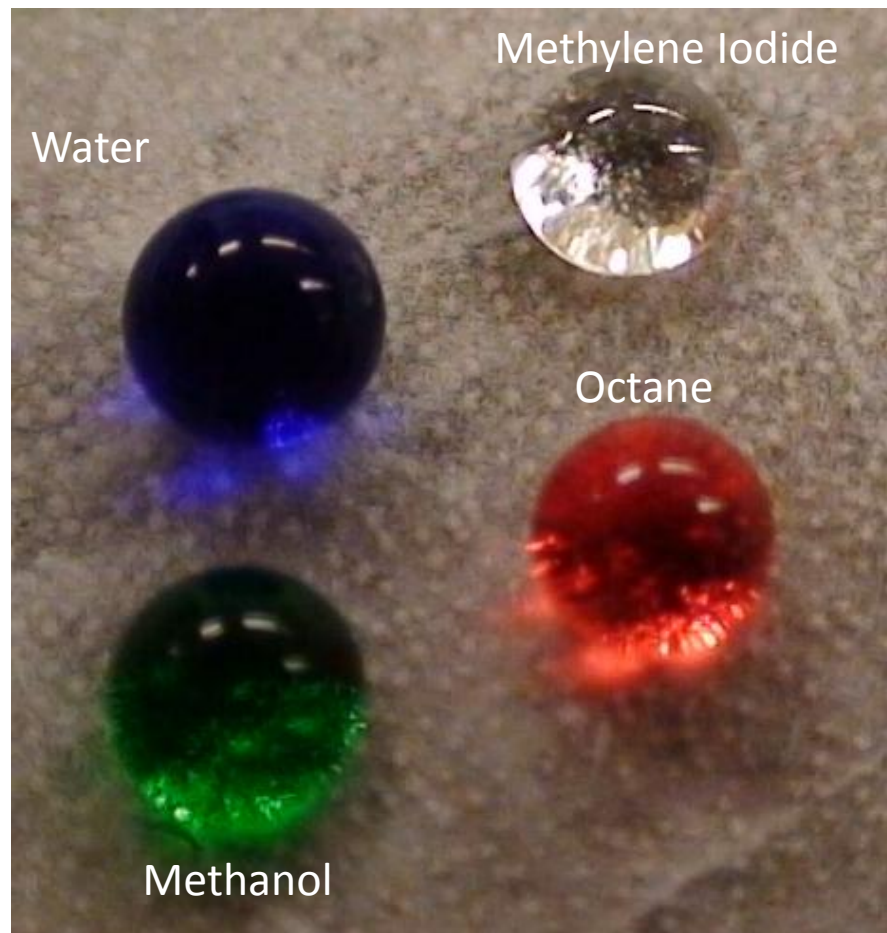
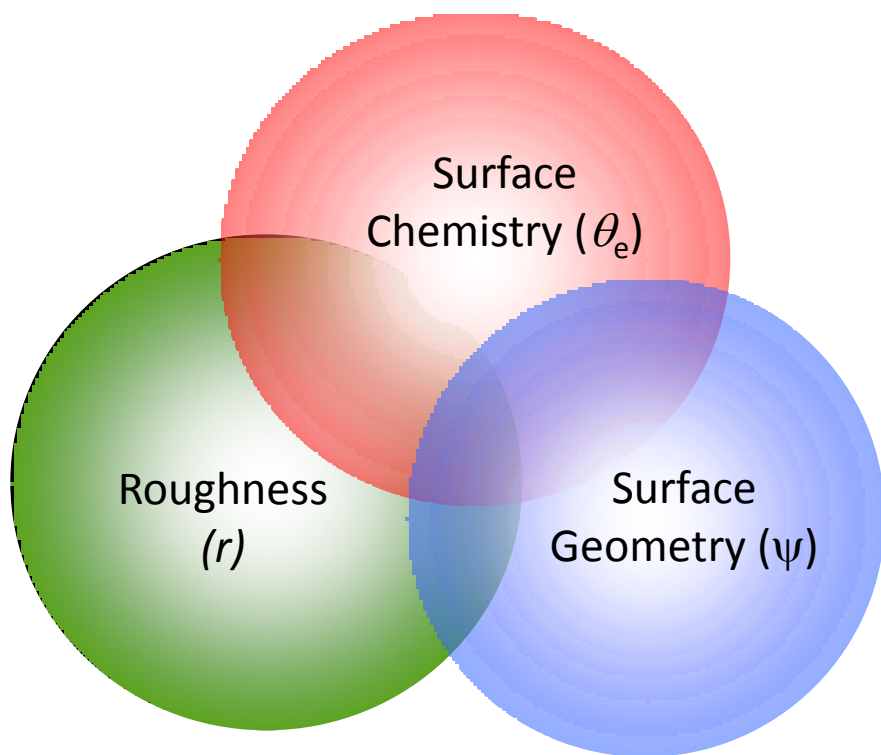
Hydrophobic  
 $\theta > 90^\circ$



Superhydrophobic  
 $\theta^* > 150^\circ$

Similarly, superoleophobic surfaces display contact angle  $\theta^* > 150^\circ$  with oils or alkanes

- **Constructing super-repellent surfaces**
  - Three key ingredients

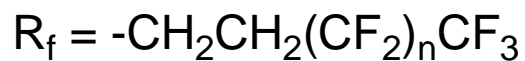
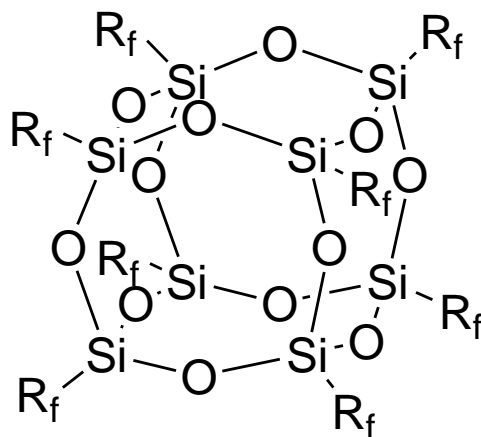
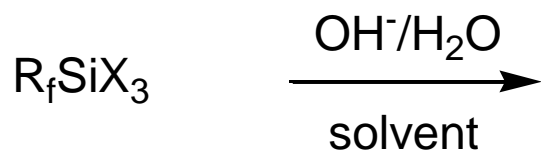


PMMA + 44 wt% POSS  
electrospun coating (beads on a string) morphology

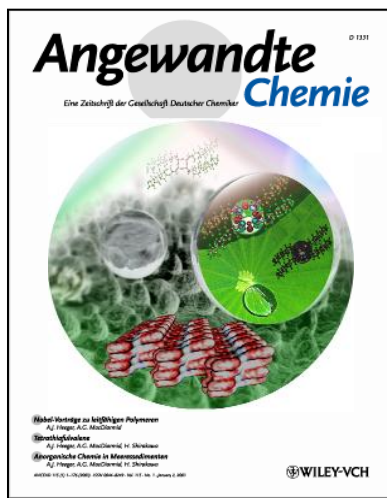
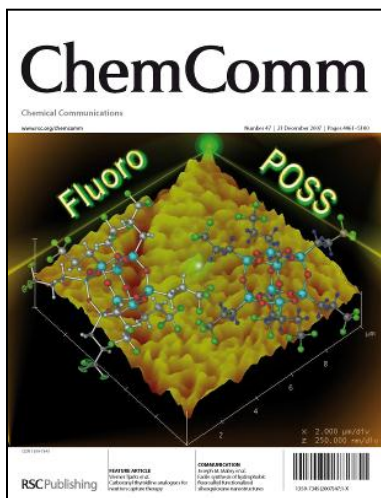
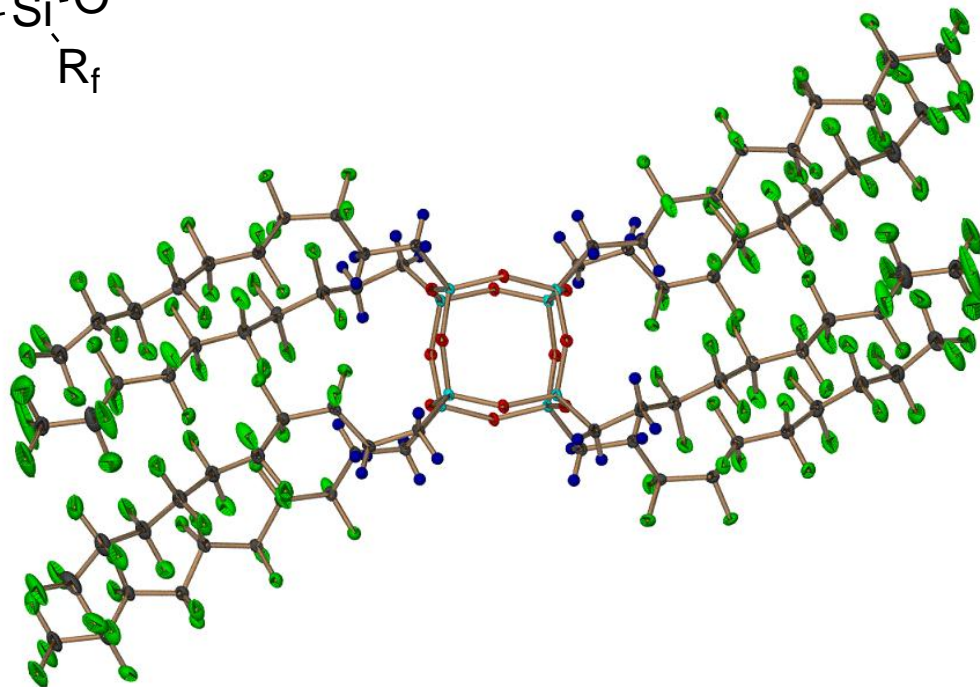




# Fluorinated POSS Synthesis

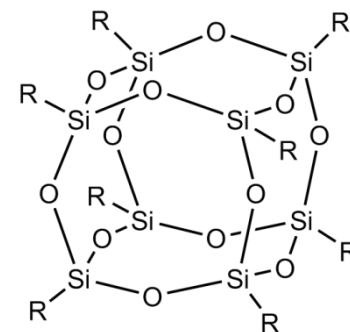
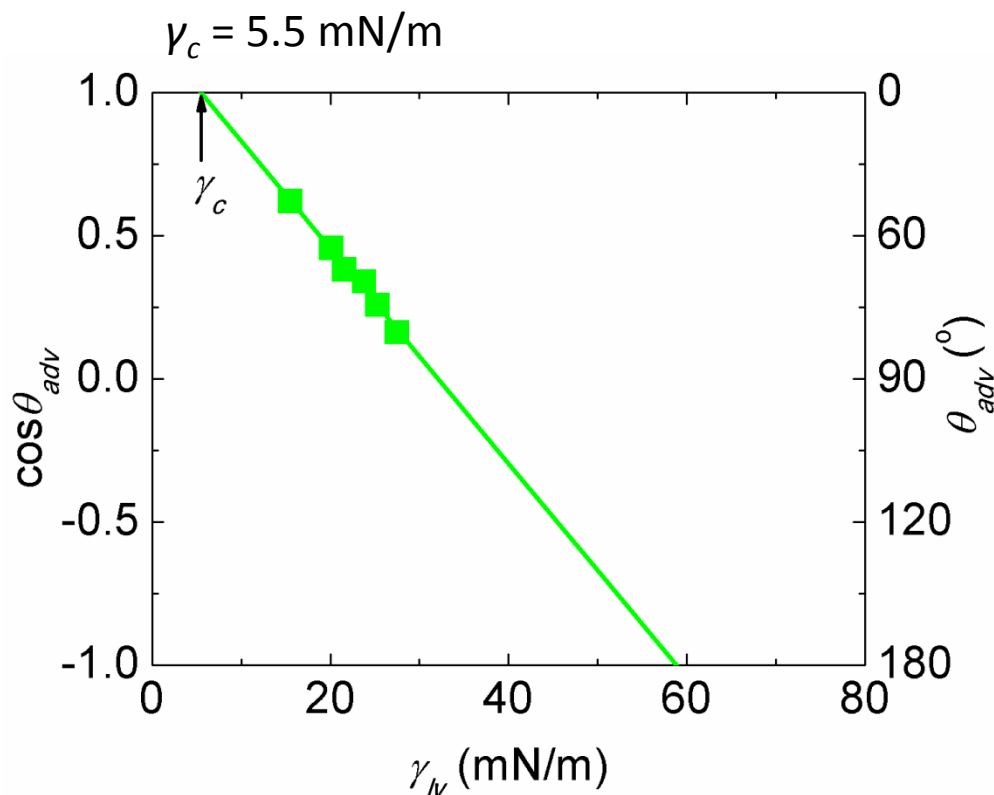


$$n = 0, 3, 5, 7$$

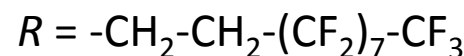




# Zisman Analysis



Fluorodecyl:



GG analysis results in surface energy calculation of:  $\gamma_c = 8 \text{ mN/m}$

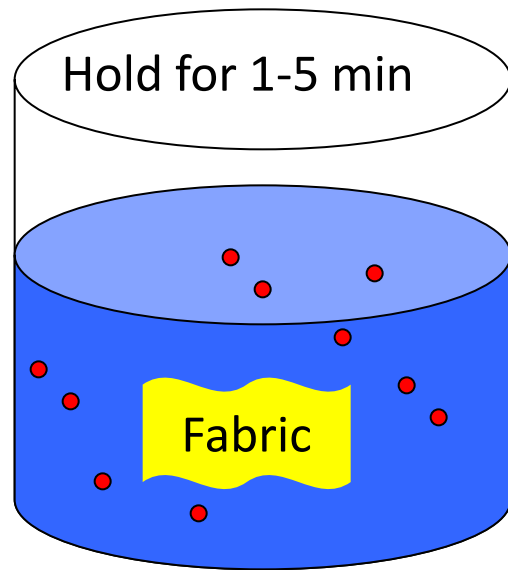
Contacting liquids:

hexadecane ( $\gamma_{lv} = 27.5 \text{ mN/m}$ ), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1) and pentane (15.5)



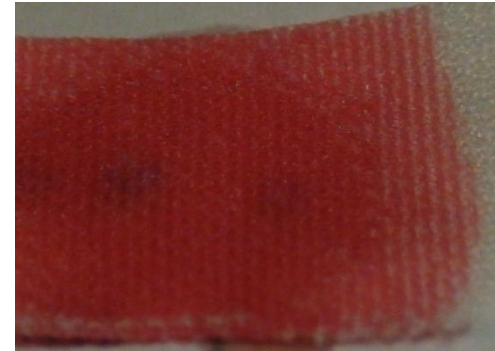
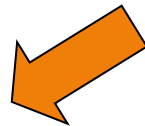
# The Dip-Coating Process

Hexadecane ( $\gamma_{lv} = 27.5 \text{ mN/m}$ ) on an as-received commercial polyester fabric



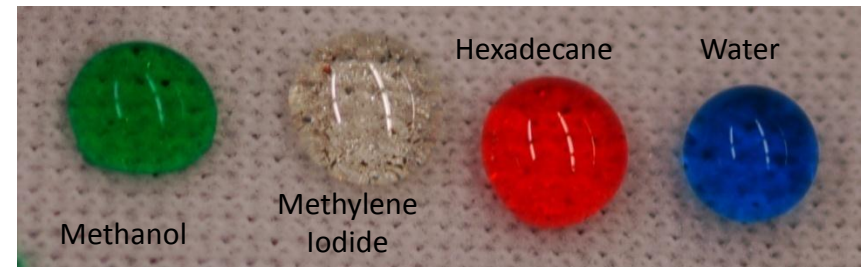
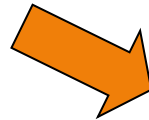
Solution of fluorodecyl POSS

Dip



Before

Dry (heat in oven at  $60^\circ \text{C}$  for 20 minutes)



After dip-coating with a solution of fluorodecyl POSS

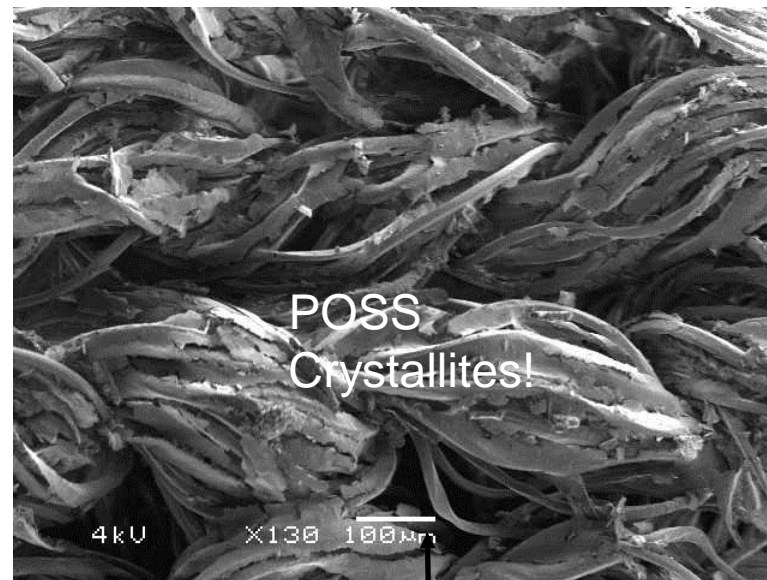




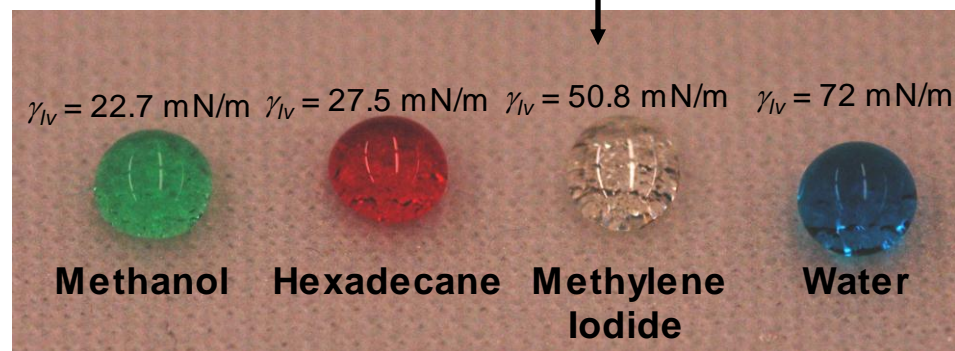
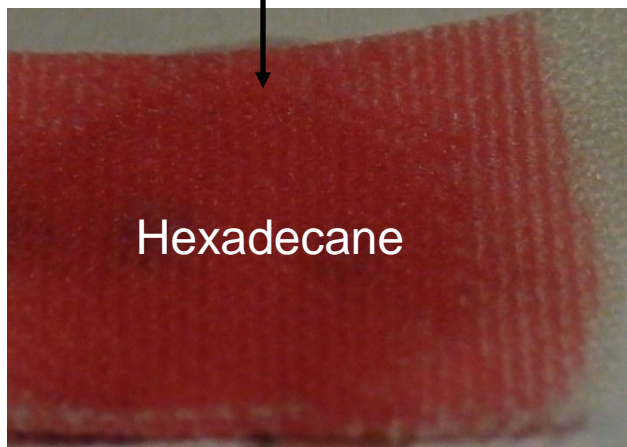
# Dip-Coated Polyester Fabric



Before coating



After coating with fluorodecyl POSS in Asahiklin (30 mg/ml)



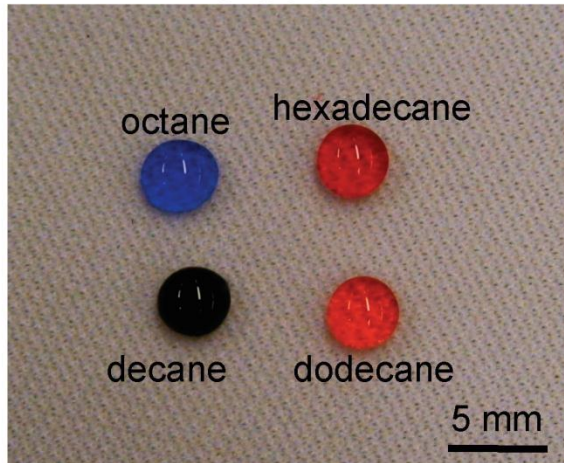




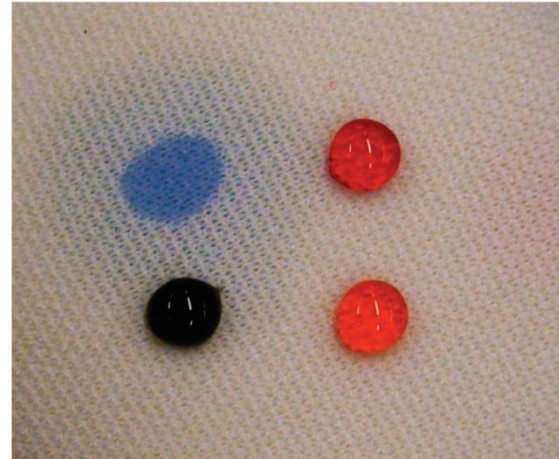
# Stretching & Surface Tension



No Strain



10% Strain



30% Strain



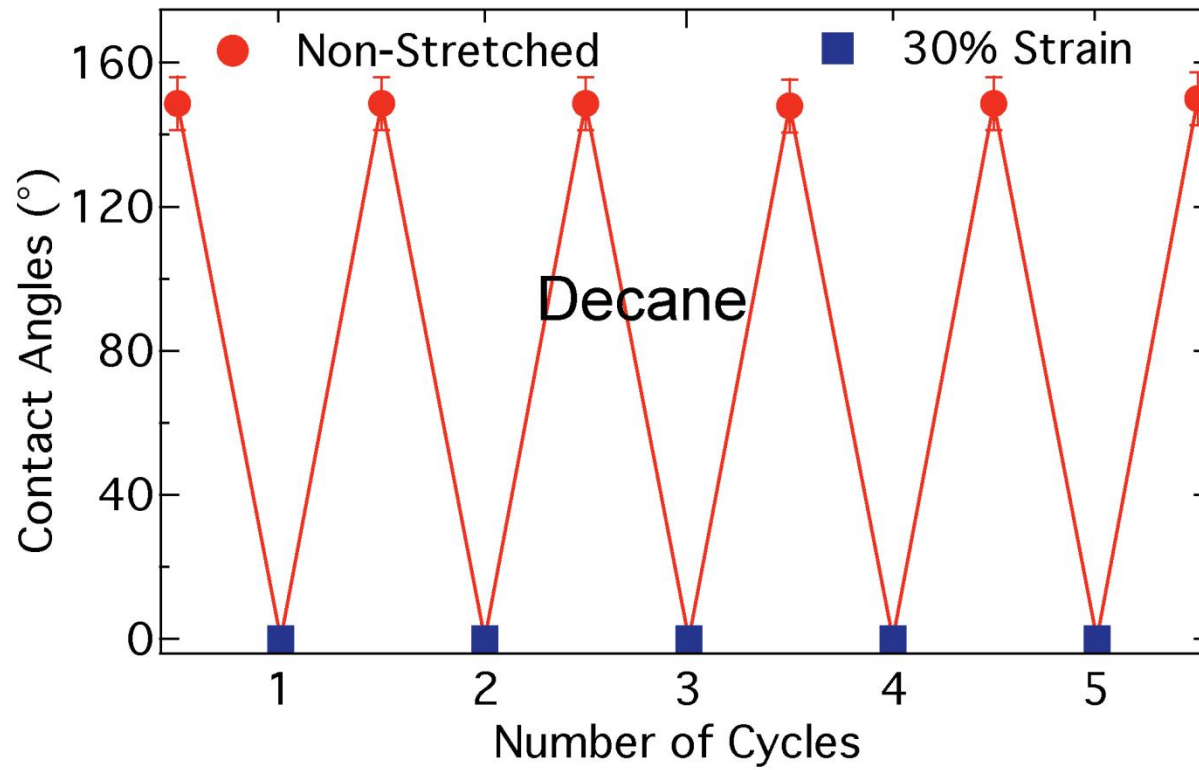
60% Strain



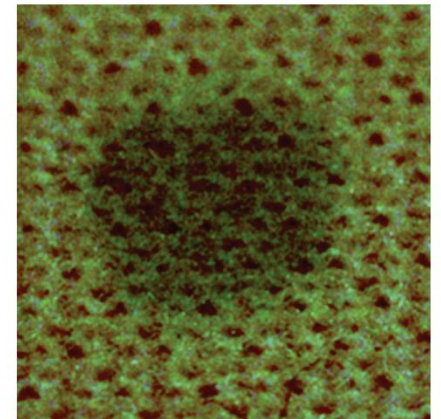
As the fabric is stretched, the liquid with the lowest surface tension (octane) passes through the fabric, while the other droplets remain beaded up on the surface. With increasing strain, liquids possessing higher and higher surface tension systematically permeate through the dip-coated fabric.



# Durability & Repeatability



Non-stretched



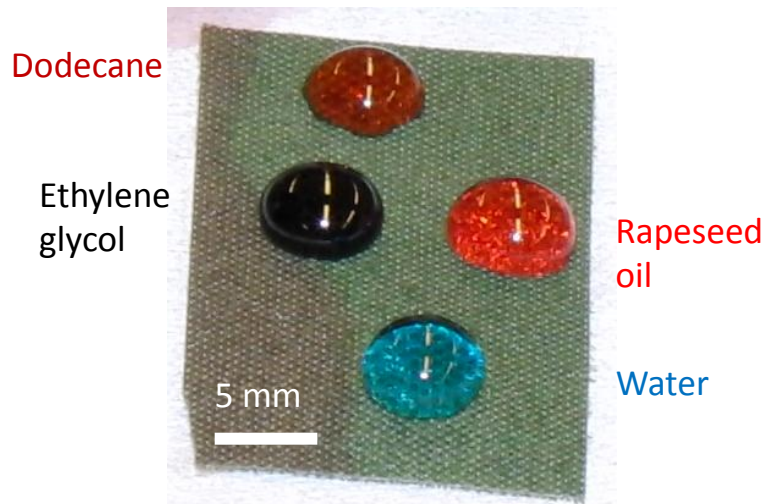
Stretched



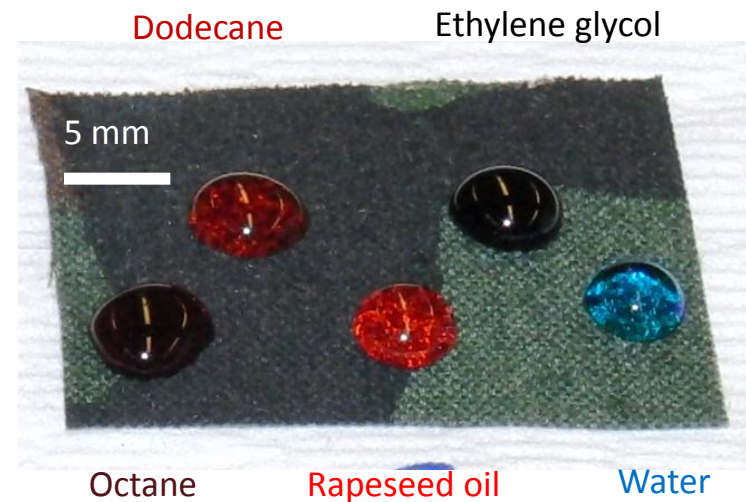


# Omniphobic fabrics

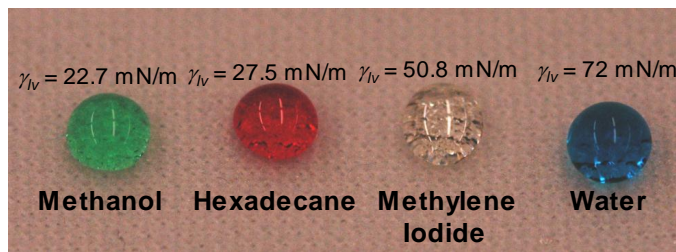
Nylon shell fabric bonded to a Gore-Tex membrane



Nomex/Kevlar/P-140 fabric



Anticon 100 polyester fabric



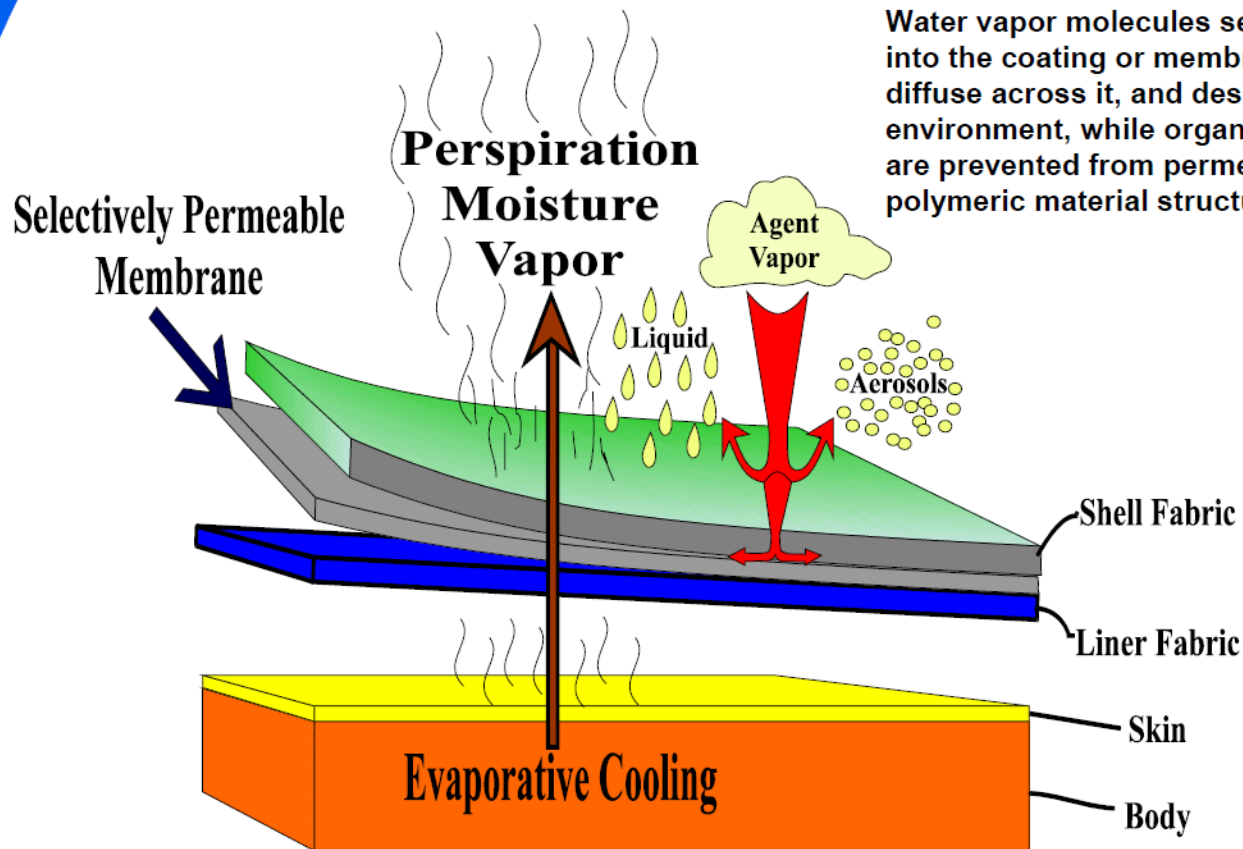
All fabrics are dip-coated with 50% POSS – 50% Tecnoflon



# Chemical Protective Clothing



## MATERIAL CONCEPT







# Icing: a Widespread Problem



Beisswenger, A. Presentation at a workshop at Wright-Patterson Air Force Base titled “*Advances in Ice Adherence and Accumulation Reduction Testing at the Anti-icing Materials International Laboratory (AMIL).*” **2008.**



# Icing Issues



- **Aircraft**
  - safety: ice may have played a role in recent Buffalo, Montana crashes
  - cost: \$1500 - \$10,000 to de-ice an aircraft<sup>1</sup>
  - increased drag, fuel consumption
  - environmental concerns: Canada banned 2-methoxyethanol
- **Power transmission equipment**
  - \$1.5 billion to replace equipment following 1998 Canadian storm<sup>2</sup>
  - \$26 million in FEMA grants for Feb 2009 Kentucky ice storm<sup>3</sup>
- **Helicopter blades, ships, windmills, locks, dams, roads, bridges, etc.**

1) Frankenstein, S. and Tuthill, A.M. *J. Cold Reg. Eng.* **2002**, 16, 83-96.

2) <http://www.cbc.ca/canada/montreal/story/2008/01/03/qc-icestorm0103.html>

3) <http://www.fema.gov/news/newsrelease.fema?id=49248>



# Current De-icing, Anti-icing Methods



- **de-icing: remove ice that has formed**
  - done prior to flight
  - spray aircraft with anti-freeze
  - issues
    - cost, time consuming, environmental concerns



- **anti-icing: prevent/reduce ice buildup during flight**
  - rubber “boots”: inflate / deflate to crack and break up ice
  - hot air from engines
  - electrically heated elements (also used on power lines)
  - mechanical “shocks” via current spike in transducer
  - pump antifreeze through small pores
  - coatings that slowly release antifreeze





# Superoleophobic Ice Release Coatings



## First major research efforts: 2007-2010

Superhydrophobic coatings with  $<80$  kPa ice adhesion demonstrated in laboratory, moderately competitive environment, addresses only some forms of icing.

- Boeing Phantom Works prevention of ice growth in truck wheel-wells.
- Boeing Commercial anti-icing coatings for the 787.
- So. Cal. Edison (SCE) anti-icing coatings for power lines.



Key advantages: Allows ice to slip off surfaces with modest levels of shear (e.g. aircraft during taxi); prevents growth of ice during “freezing rain” events

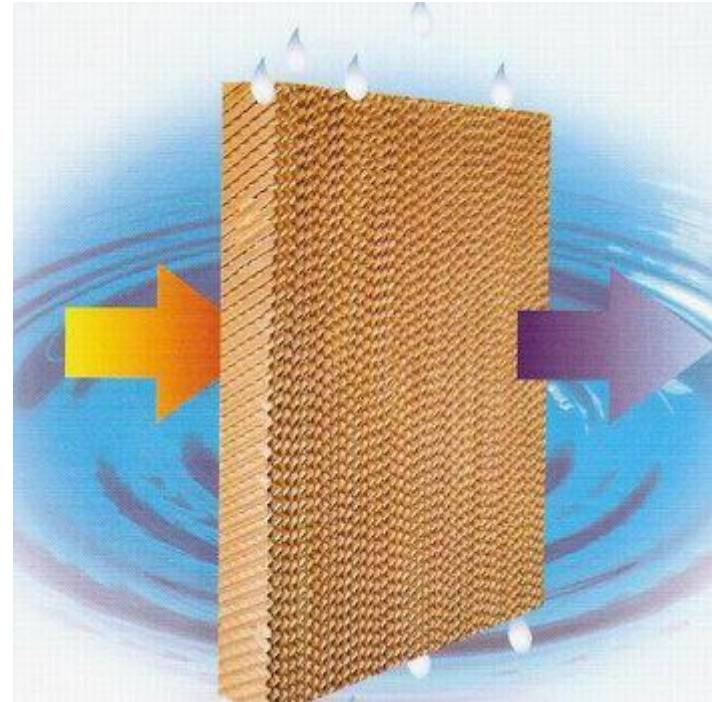




# Underwater anti-fouling

**Currently under laboratory investigation,** Superoleophobic coatings allow dirt to slide off of underwater surfaces readily; prevents build-ups that lead to fouling

LBNL: Cooling tower packings



Advantages: Greatly decreased maintenance costs; energy savings for buildings



# Oil / Water Separation



## First Laboratory Demonstration in 2010

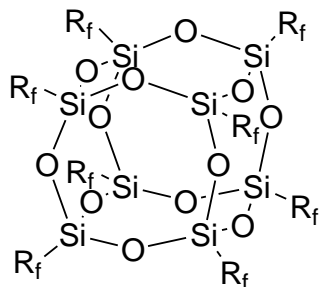
Can separate any immiscible fluid that is selectively absorbed into polymers (includes sea water, methanol, ethanol). No competition for low fouling, gravity driven, separation of emulsions. Demonstrated on multi-liter scale / hundreds of hours of operation.



Advantages: Increased reliability of fuel delivery; decreased monitoring costs. Can be gravity driven. Compact and lightweight. Easy to construct.

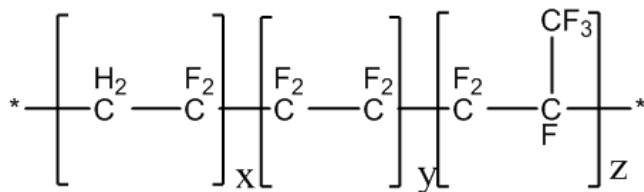


# Dip-coating process for conformal coating of textured surfaces



$R_f = -CH_2-CH_2-(CF_2)_7-CF_3$   
Fluorodecyl POSS

$\gamma_{sv} \approx 8 \text{ mN/m}$



**Tecnoflon® (BR9151)**

Fluoro-elastomer from  
Solvay-Solexis

$\gamma_{sv} \approx 18 \text{ mN/m}$

Anticon 100 polyester fabric



Before Dip-coating

200 μm

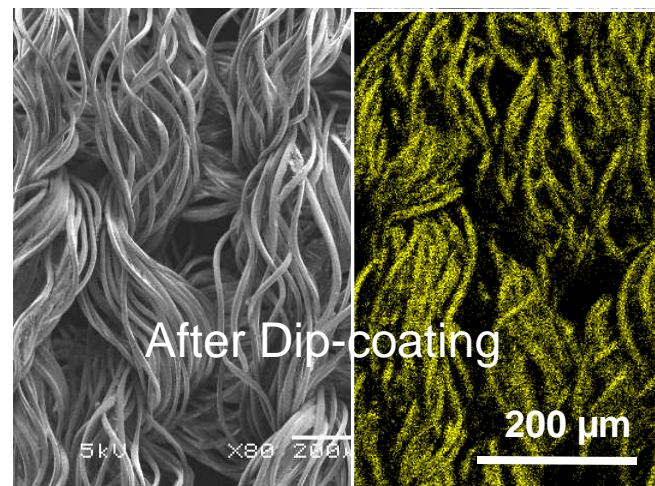
50:50 mixture, total solids = 10 mg/ml

Dip in Asahiklin solution for 5 minutes

Air dry to remove solvent

Heat treat at 60 °C for 30 minutes

EDAXS spectrum for fluorine



After Dip-coating

200 μm

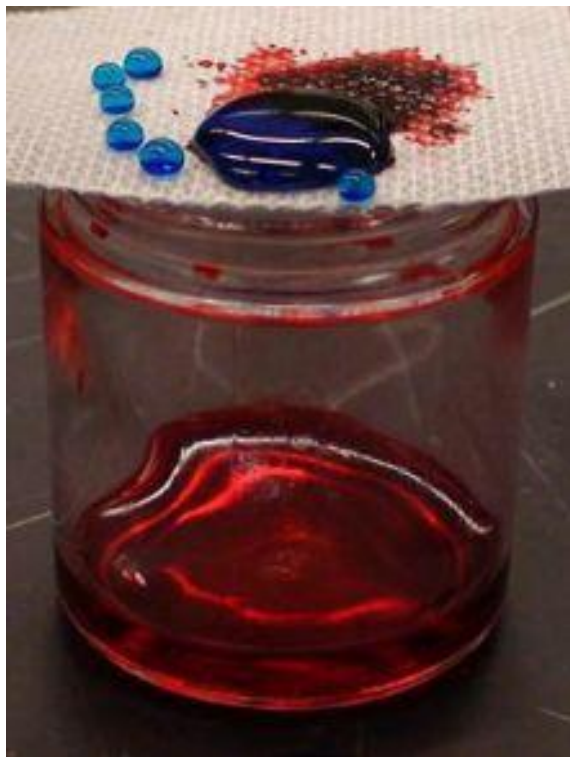




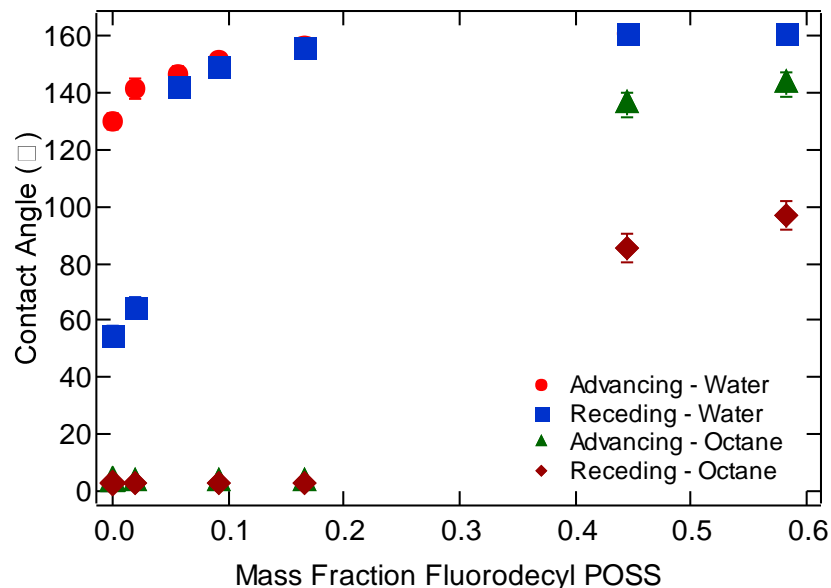
# Superhydrophobic/Superoleophilic

## Designing Superoleophobic Surfaces

Anish Tuteja,<sup>1</sup> Wonjae Choi,<sup>2</sup> Minglin Ma,<sup>1</sup> Joseph M. Mabry,<sup>3</sup> Sarah A. Mazzella,<sup>3</sup> Gregory C. Rutledge,<sup>4</sup> Gareth H. McKinley,<sup>2\*</sup> Robert E. Cohen<sup>1\*</sup>



**Superhydrophobic  
Superoleophilic**



At low POSS concentrations many surfaces are *both* superhydrophobic and superoleophilic ( $\theta_{alkane}^* \approx 0^\circ$ ). Thus, these porous surfaces form ideal membranes for separating mixtures / dispersions of alkanes (oils) and water

*Science*, **2007**, 318, 1618.



# PEGDA + Fluorodecyl POSS

Can hydrogen bond with water

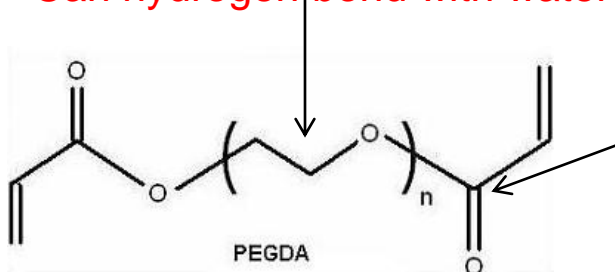


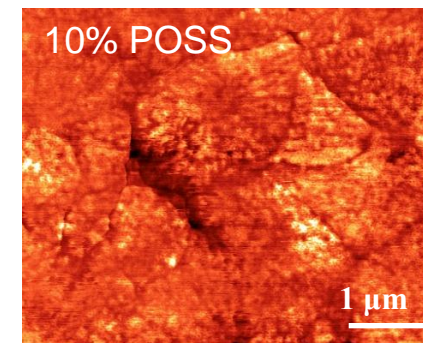
Photo-crosslinkable

AFM Phase images of spin-coated PEGDA + POSS films

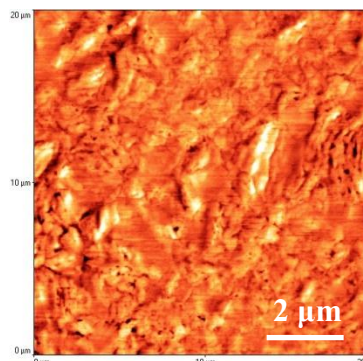
Pure PEGDA



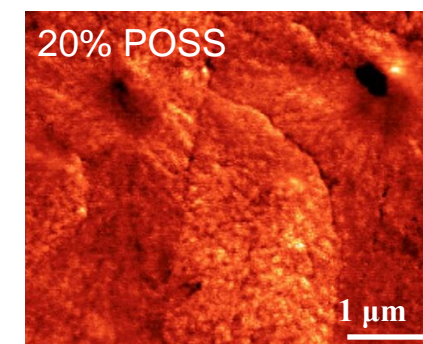
10% POSS



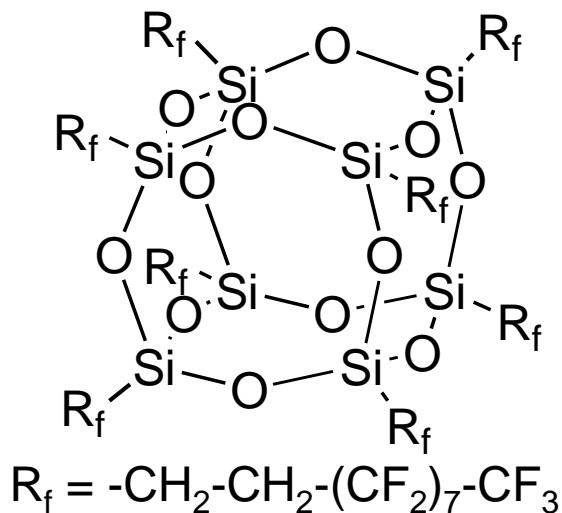
20% POSS  
Under water



20% POSS



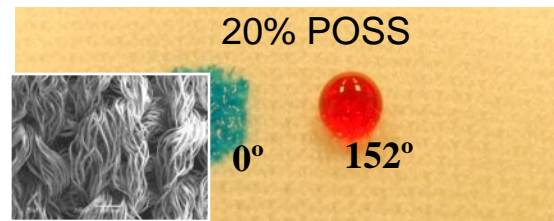
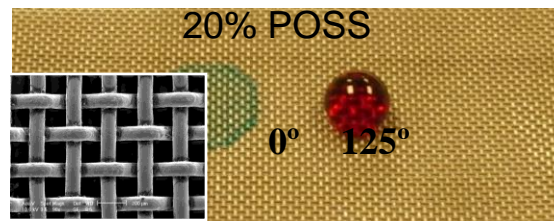
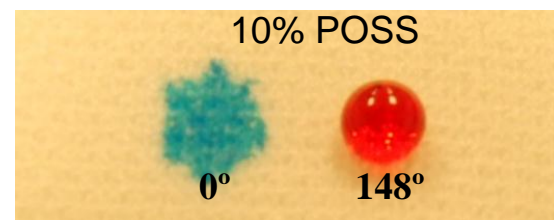
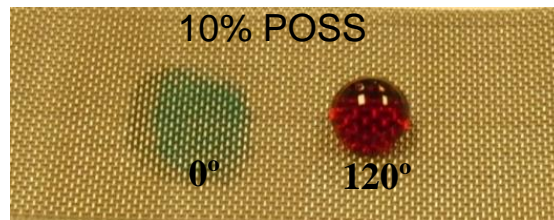
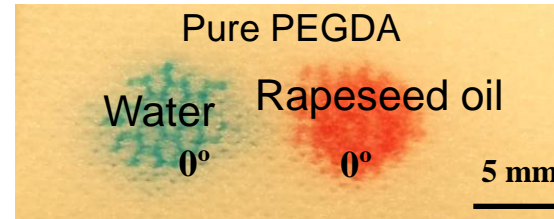
Fluorodecyl POSS molecules preferentially segregate to the air interface and crystallize.



Fluorodecyl POSS

$$\gamma_{sv} \approx 8 \text{ mN/m}$$

Surfaces with inherent re-entrant curvature **dip-coated** with PEGDA + POSS blends



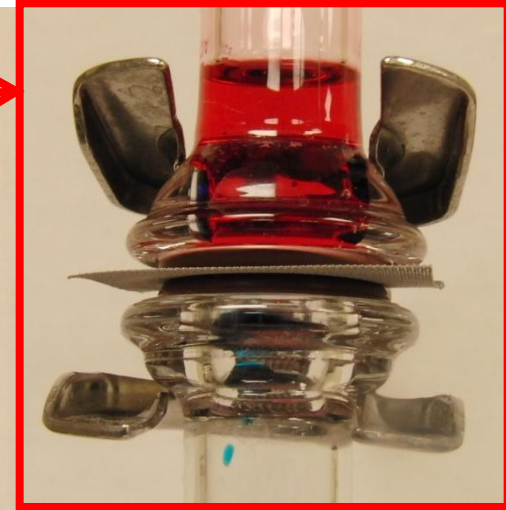
Stainless Steel Wire Mesh

Commercial Polyester Fabric

PEGDA surface reconfiguration leads to superhydrophilic behavior.

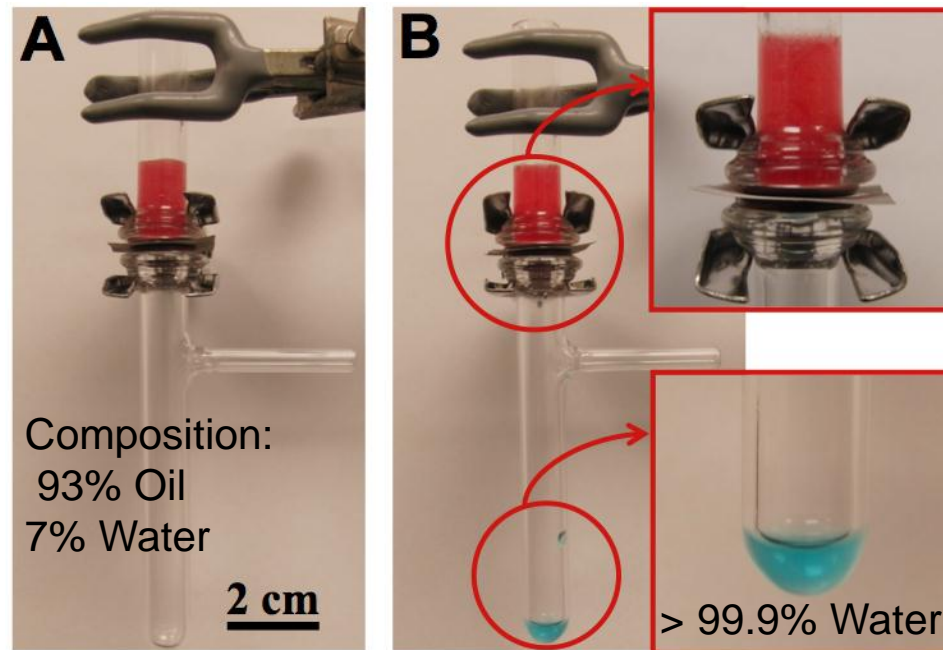
# Free oil – water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.

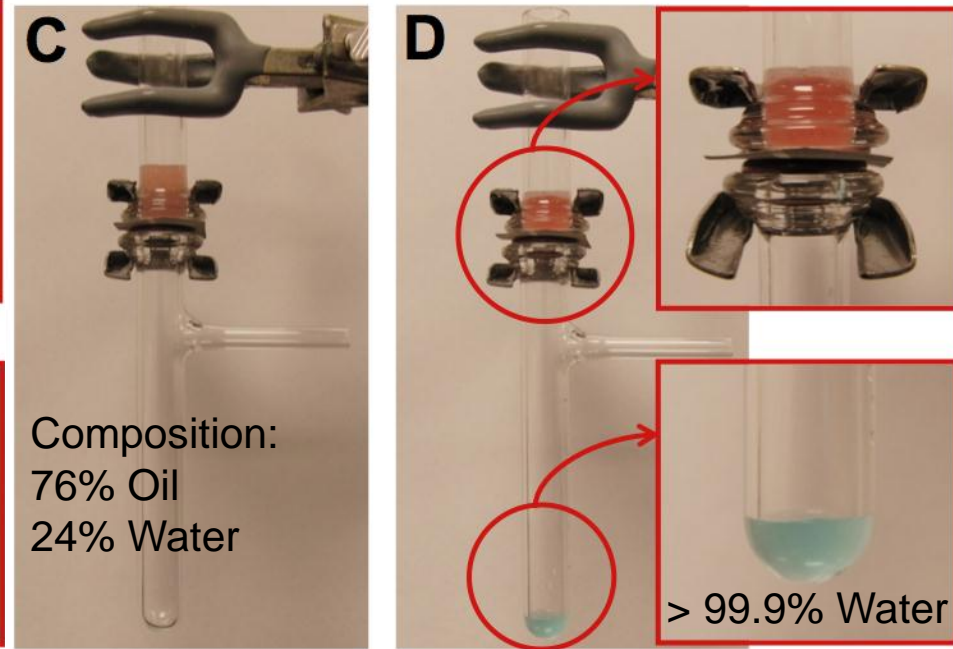




## Water-in-Oil Emulsion



## Oil-in-Water Emulsion

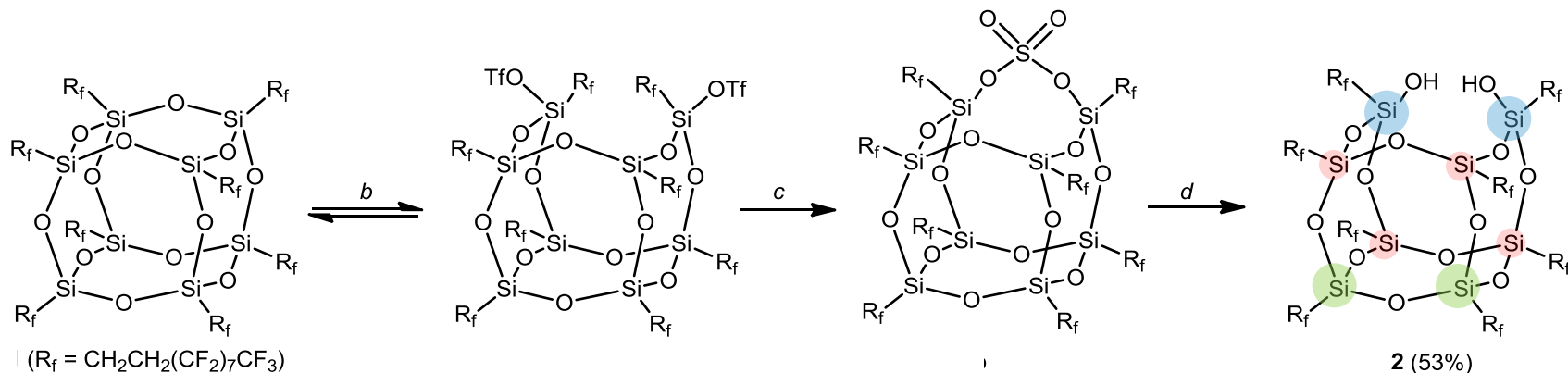


A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.



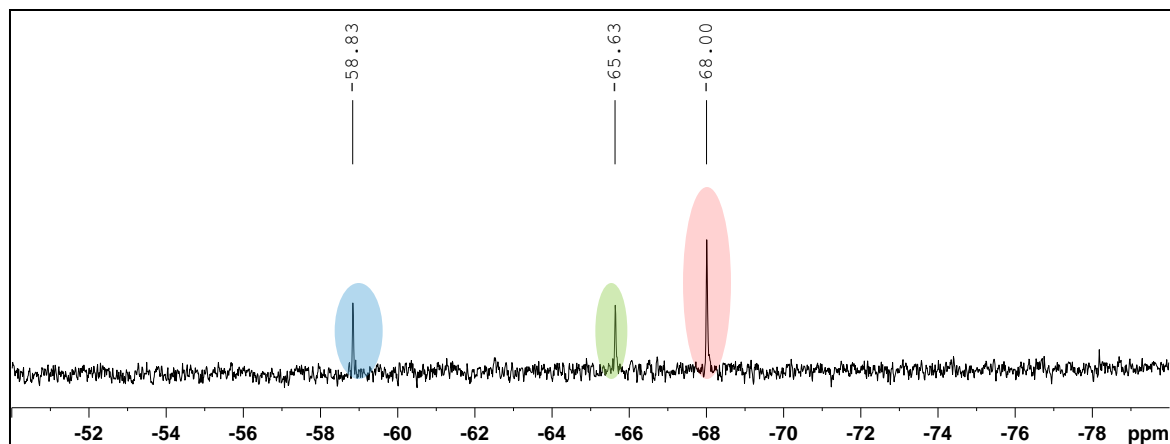


# Incompletely Condensed Silsesquioxane (Next Generation)



<sup>a</sup>Conditions: All reactions were performed in C<sub>6</sub>F<sub>6</sub> at 25 °C. <sup>b</sup>CF<sub>3</sub>SO<sub>3</sub>H, 75 mins. <sup>c</sup>NBut<sub>4</sub>HSO<sub>4</sub>, 30 mins, <sup>d</sup>(CF<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OH/H<sub>2</sub>O (10:1), 12 hrs.

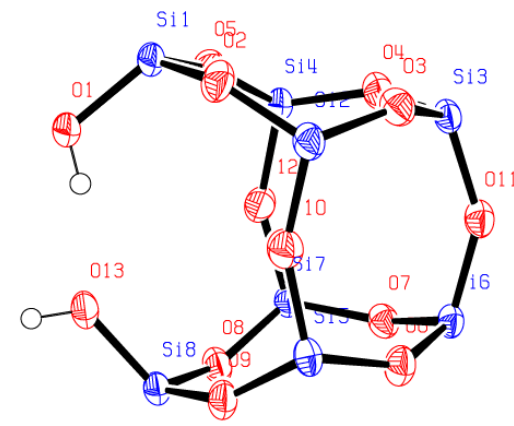
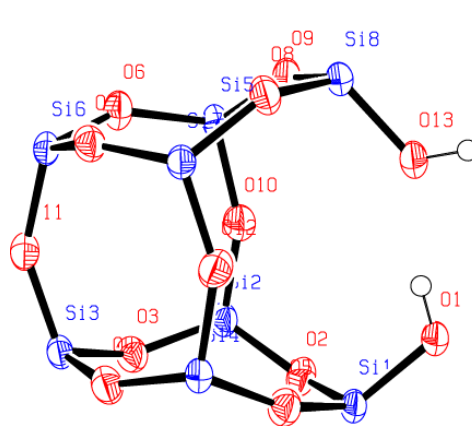
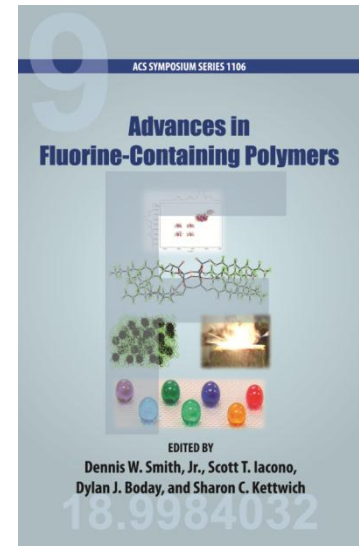
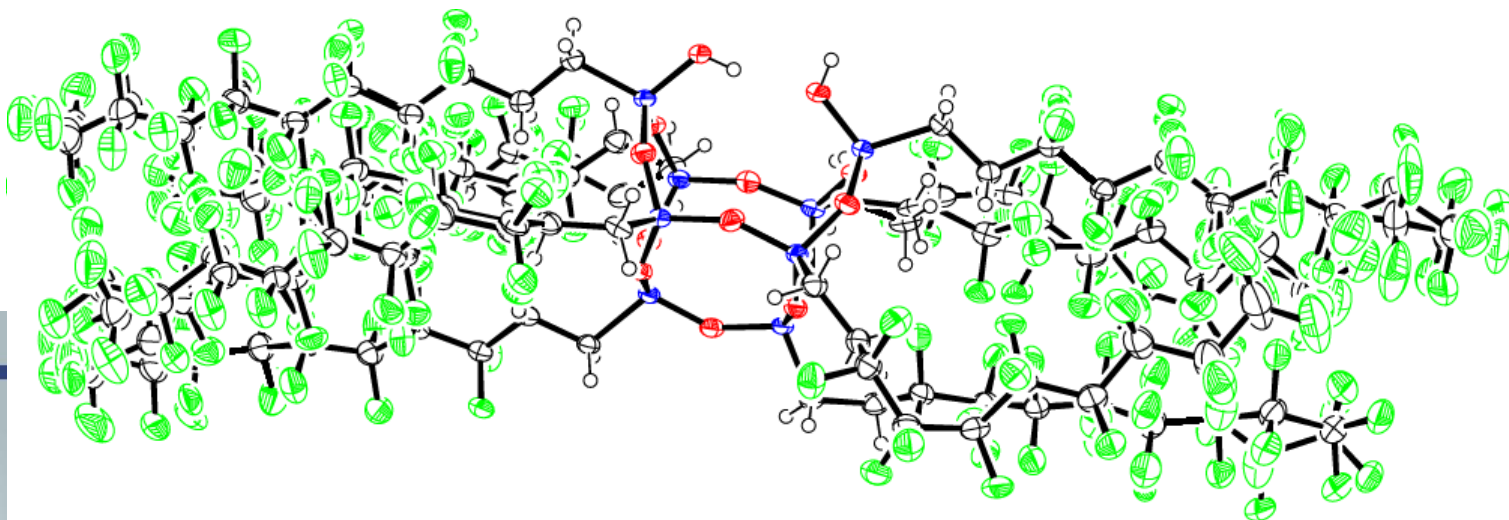
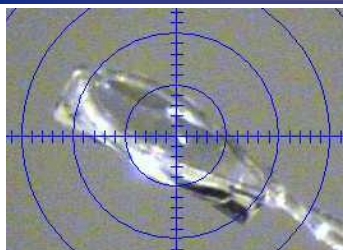
<sup>29</sup>Si NMR in C<sub>6</sub>F<sub>6</sub> of disilanol F-POSS



- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.

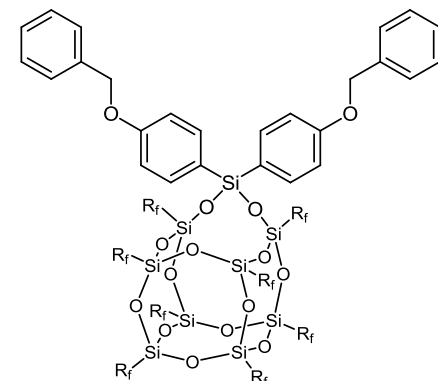
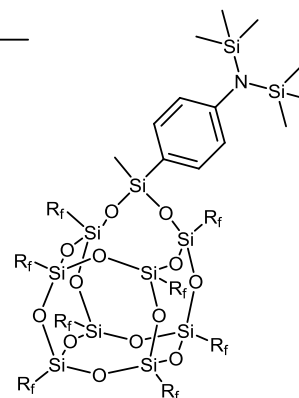
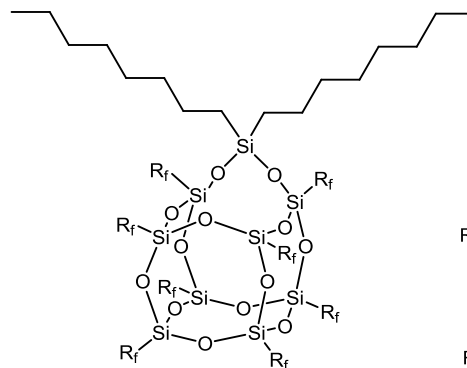
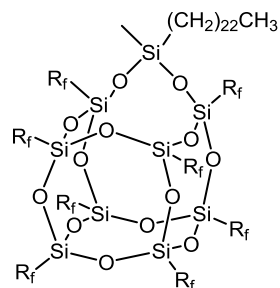
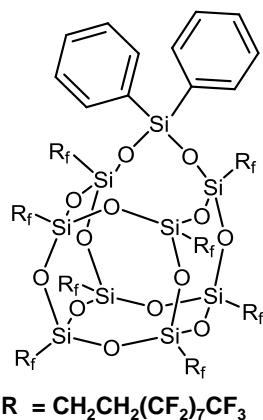
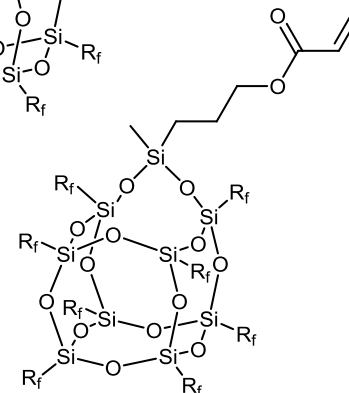
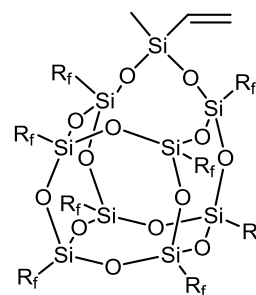
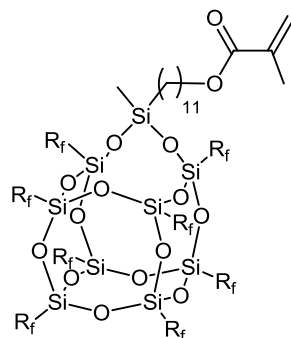
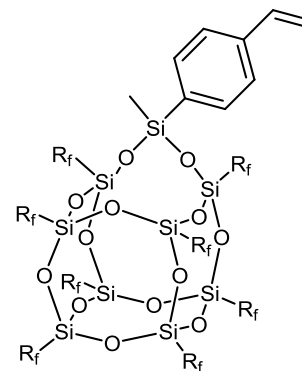
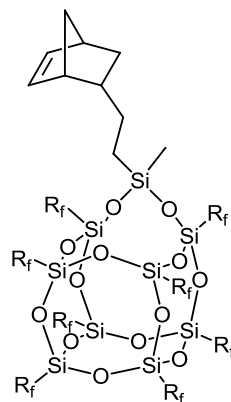
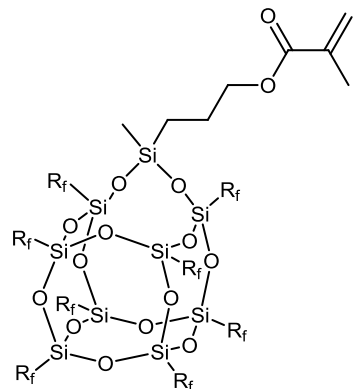


# X-Ray Crystal Structure of Disilanol



- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- $M_r$ =, monoclinic, space group  $P2(1)/c$ ,  $a=11.84(10)$  Å,  $b=57.11(6)$  Å,  $c=19.06(2)$  Å,  $\alpha=90.00^\circ$ ,  $\beta=92.21(10)^\circ$ ,  $\gamma=90.00^\circ$ ,  $V=12878(2)$  Å<sup>3</sup>

# F-POSS Structures Synthesized





# Summary



- **FluoroPOSS are superhydrophobic.**
- **FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic (omniphobic).**
- **Membranes can be tuned to separate oil from water and water from oil.**
- **For the first time, superhydrophilic and superoleophobic surfaces have been developed**
- **Such surfaces are ideal for the separation of both free-oil and oil-water emulsions.**
- **These membranes, for the first time, allow continuous-flow oil-water emulsion separation.**
- **Applications in anti-icing, anti-fouling and other coatings offer reduction in energy cost.**



# QUESTIONS?

